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XLIII. *On the Atomic Volume and Crystalline Condition of Bodies, and on the Change of Crystalline Form by means of Heat.* *By* Dr. HERMANN KOPP*.

IN a former paper (Poggendorff, *Ann.* xlvii.) I have endeavoured to show that a relation subsists between the vou mes in which bodies unite in forming chemical compounds, in addition to that which is known to exist with respect to their weights. Gay-Lussac had already shown that gaseous compounds combine with one another according to volumes; but this observation had not been extended to solid or liquid compounds. Hence the object of my inquiries was to examine the *atomic volumes* in which the latter combine, in contradistinction to their *atomic weights*; to which attention had hitherto been exclusively directed in examining their chemical composition.

The numbers representing the atomic volumes of bodies are proportional, just as the atomic weights are; and the atomic volume of any body may be deduced from its atomic weight, merely by dividing the latter by its specific gravity. But it is evident that these numbers must vary according to the system of atomic weights adopted; hence in the following paper, that scale of equivalents in which oxygen is equal to 100 is adopted, and not what is still retained by a few chemists, in which hydrogen is regarded as unity. The formulas of the compounds examined are generally those of Berzelius.

It is not sufficient to affirm that bodies unite according to their respective atomic weights and volumes: we must also comprehend clearly what is meant by the application of these terms. Nor is this difficult; for the idea of *mass* is represented by atomic *weight*; whilst a regular and definite *volume* is evidently represented by a *crystal*.

The doctrine of isomorphism shows us that there are many bodies which possess an analogous constitution and the same crystalline form. Our idea of the *volume* (or in other words of the crystalline form) of these bodies must, therefore, be the same. From this it follows that their specific weight is dependent upon our idea of *mass* (that is of atomic weight), whilst our idea of specific weight is connected with the mass contained in the same volume. From these considerations the following law may be deduced:

The specific weight of isomorphous bodies is proportional to their atomic weight; or, isomorphous bodies possess the same atomic volume.

* Communicated by the Author.

This law may be proved from facts already known. The following presents a tabular view of all the isomorphous groups, the specific gravities of which have been determined with accuracy. In the first column the chemical formulas of the compounds are stated; in the second their specific gravities, with the authorities from which they are taken; in the third the atomic weights adopted by Berzelius; and in the fourth the atomic volumes deduced from the observations.

Gold and Silver.

Au	19·258	Brisson	1243·0	64·54
Ag	10·428	Karsten.	1351·6	129·61
			675·8	64·80

Berzelius has given the number 1351 as the atomic weight for silver, but Regnault has lately proved that 675 is more correct.

Potassium and Sodium.

K	0·865	Gay-Lussac and Thénard	489·92	566·39
Na	0·972	,, ,, ,,	290·90	299·27
			581·80	598·54

Dr. Clarke, influenced by several theoretical considerations, was induced a few years since to propose that the atomic weight of sodium should be raised twice as high as it is considered by Berzelius to be; and it is remarkable, that we obtain an equal atomic volume between potassium and sodium, if we adopt the view of Dr. Clarke.

Oxide of Tin and Titanic Acid.

SnO_2	6·960	Mohs	935·20	134·38
TiO_2	4·202	Breithaupt	503·69	119·87
	4·254			118·40
	4·249	Mohs		118·54
	3·759	Breithaupt		134·00
	3·826	Mohs		131·65

The first three numbers for the specific gravity of titanic acid are deduced from the mineral *rutile*, which is always rendered impure by substances specifically heavier; its atomic volume must, therefore, be smaller than it really is. The two last are drawn for *anatase*.

Alumina, Peroxide of Iron, Oxide of Chromium and Ilmenite.

Al_2O_3	3·909	Mohs	642·33	164·32
	3·979			161·43
	3·995	Breithaupt		160·78
	4·023			159·67
	3·562	Musschenbroek		180·33
	3·531	Brisson		181·93
Fe_2O_3	5·225	Boullay	978·43	187·26
	5·24	Leonhard		186·72
	5·30			184·61
	5·251	Mohs		186·33

Cr_2O_3	5·21	Wöhler	1003·6	192·63
$(Fe+Ti)O_3$	4·729	Breithaupt	942·90	199·39
	4·793			196·72
	4·75	Kupffer		198·51
	4·78			197·26

Spinel, Gahnite, Chrome-iron ore, Franklinite and Magnetic-iron-ore.

MgO, Al_2O_3	3·48	Breithaupt	900·68	258·82
	3.62			248·81
$\frac{1}{2}\left(\begin{matrix}ZnO, Al_2O_3 \\ FeO, Al_2O_3\end{matrix}\right)$	4·232	Mohs	1113·6	263·12
$\frac{1}{2}\left(\begin{matrix}MgO, Al_2O_3 \\ FeO, Cr_2O_3\end{matrix}\right)$	4·410	Abich	1171·8	265·71
	4·439			263·97
$\frac{1}{2}\left(\begin{matrix}ZnO, Fe_2O_3 \\ MnO, Fe_2O_3\end{matrix}\right)$	5·091	Mohs	1453·0	285·41
FeO, Fe_2O_3	5·094	Mohs	1417·6	278·28

Copper-glance and Silver-copper-glance.

Cu_2S	5·695	Mohs	992·56	174·28
	5·735			173·07
$(Cu+Ag)S$	6·255	Stromeyer	1272·7	203·47

The atomic weight of silver is supposed to be half that adopted by Berzelius.

Antimony-glance and Orpiment.

Sb_2S_3	4·620	Mohs	2216·4	479·75
	4·626	Breithaupt		479·11
	4·850	Musschenbroek		456·99
As_2S_3	3·313	Musschenbroek	1543·6	465·91
	3·480	Mohs		443·55
	3·459	Karsten		446·24

Cobalt-glance and Nickel-glance.

CoS_2+CoAs_2	6·298	Mohs	2080·4	330·32
NiS_2+NiAs_2	6·238	Breithaupt	2081·8	333·72
	6·331			328·83

Arsenic- and Antimony-ruby-blende.

$Ag_3S_3+As_2S_3$	5·531	Breithaupt	6201·9	1121·3
	5·592			1109·1
	5·524	Mohs		1122·7
$Ag_3S_3+Sb_2S_3$	5·787	Breithaupt	6874·7	1187·9
	5·844			1176·4
	5·831	Mohs		1179·0

Tennantite and black Copper.

$\begin{matrix}Cu_6S_3As_2S_3 \\ +2(Cu_6S_3As_2S_3)\end{matrix}$	4·375	Phillips	13563·7	3100·3
$\begin{matrix}Cu_6S_3, Sb_2S_3 \\ +2(Pb_3S_3, Sb_2S_3)\end{matrix}$	5·763	Mohs	18600·9	3227·6

Lead-glance and Seleniuret of Lead.

Pb S......	7·220	Musschenbroek	1495·7	207·16
	7·587	Brisson		197·13
Pb Se......	8·20	Leonhard	1789·1	218·18
	8·80			203·30

The Carbonates of Zinc and Magnesia; Mesitine; the Carbonates of Iron and Manganese; Dolomite and Calcareous spar.

$Zn O, C O_2$	4·442	Mohs	779·67	175·52
	4·4	Naumann		177·20
	4·5			173·26
$Mg O, C O_2$	2·208	Breithaupt	534·79	190·45
	3·001	Mohs		178·20
	3·112			171·85
	2·88	Naumann		185·69
	2·97			180·06
$\frac{1}{2}\left\{\begin{matrix} Mg O, CO_2 \\ Fe O, C O_2 \end{matrix}\right\}$	3·350	Mohs	625·22	186·62
	3·363			185·90
$Fe O, C O_2$	3·829	Mohs	715·65	186·90
	3·872	Naumann		184·82
	3·6	Naumann		198·79
	3·9			183·50
$Mn O, C O_2$	3·550	Mohs	722·34	203·48
	3·592			201·10
$\frac{1}{2}\left(\begin{matrix} Mg O, CO_2 \\ Ca O, C O_2 \end{matrix}\right)$	2·884	Mohs	583·62	202·36
$Ca O, C O_2$	2·721	Mohs	632·46	232·43
	2·750	Naumann		229·98

Arragonite, Strontianite, Witherite and Carbonate of Lead.

$Ca O, C O_2$	2·931	Mohs	632·46	215·78
	2·995	Breithaupt		211·17
$Sr O, C O_2$	3·605	Mohs	923·73	256·24
	3·625	Karsten		254·82
$Ba O, C O_2$	4·302	Karsten	1233·3	286·68
	4·301	Mohs		286·75
$Pb O, C O_2$	6·465	Mohs	1670·9	258·46
	6·428	Karsten		259·94

The Sulphates of Barya, Strontia and Lead.

$Ba O, S O_3$	4·200	Karsten	1458·1	347·15
	4·446	Mohs		327·95
$Sr O, S O_3$	3·588	Karsten	1148·5	320·08
	3·953	Breithaupt		290·52
$Pb O, S O_3$	6·169	Karsten	1895·7	307·29
	6·298	Mohs		301·00

The Nitrates of the same Oxides.

$Ba O, N_2 O_5$	2·915	Hassenfratz	1633·9	560·51
	3·185	Karsten		513·00

SrO, N_2O_5	2·890	Karsten	1324·3	458·25
	3·006	Hassenfratz		440·57
PbO, N_2O_5	4·400	Karsten	2071·5	470·80
	4·769	Breithaupt		434·37

The Chlorides of Barium, Strontium and Lead.

$BaCl_2$	3·860	Boullay	1299·5	336·66
	3·704	Karsten		350·84
$SrCl_2$	2·803	Karsten	989·9	353·18
$PbCl_2$	5·802	Karsten	1737·2	299·40
	5·682			305·72
	5·238	Monro		331·60

The Nitrates of Potash and Ammonia.

KO, N_2O_5	1·933	Watson	1267·0	655·47
	2·101	Karsten		603·04
	2·058	Kopp		615·64
N_2H_8O, N_2O_5	1·707	Kopp	1004·0	588·16
	1·579	Hassenfratz		635·84

The Chlorides of Potassium and Ammonium.

KCl_2	1·915	Karsten	932·57	486·99
	1·945	Kopp		479·47
$N_2H_8Cl_2$	1·450	Watson	669·61	461·81
	1·528	Mohs		438·24
	1·500	Kopp		446·41

The Carbonates of Soda and Silver.

NaO, CO_2	2·466	Karsten	667·34	276·86
AgO, CO_2	6·077	Karsten	172·81	284·36

The Sulphates of the same.

NaO, SO_3	2·631	Karsten	892·06	339·05
	2·462	Mohs		362·33
AgO, SO_3	5·341	Karsten	1952·8	365·65

The Nitrates of the same.

NaO, N_2O_5	2·256	Karsten	1067·9	473·35
	2·188	Marx		488·07
	2·096	Klaproth		509·50
	2·200	Kopp		485·43
AgO, N_2O_5	4·355	Karsten	2128·7	488·79

The Chlorides of Sodium and Silver.

$NaCl_2$	2·078	Karsten	733·55	353·01
	2·150	Kopp		341·18
$AgCl_2$	5·501	Karsten	1794·3	326·18
	5·458			328·75
	5·130	Herapath		349·50

The Molybdate of Lead, the Tungstates of Lead and Lime.

PbO, MoO_3	6·7	Gmelin	2293·0	342·25
	6·698	Leonhard		342·35
	6·760	Mohs		339·20
PbO, WO_3	8·10	Leonhard	2877·7	355·27
	8·0	Gmelin		359·72
CaO, WO_3	6·040	Karsten	1839·2	304·50
	5·800	Meissner		317·10
	6·028	Meissner		305·11
	5·576	Meissner		329·85

Olivenite and Libethenite.

$Cu_4O_4, As_2O_5+2H_2O$	4·281	Bournon	3647·8	852·08
$Cu_4O_4, P_2O_5+2H_2O$	3·6	Mohs	3100·1	861·14
	3·8			815·82

The crystallized Sulphates of Zinc, Magnesia and Nickel.

ZnO, SO_3+7H_2O	2·036	Mohs	1791·8	880·06
MgO, SO_3+7H_2O	1·751	Mohs	1546·9	883·42
	1·674	Kopp		924·06
NiO, SO_3+7H_2O	2·037	Kopp	1758·2	863·14

The crystallized Sulphates of Copper and Manganese.

CuO, SO_3+5H_2O	2·274	Kopp	1569·3	690·10
	2·2	Gmelin		713·32
MnO, SO_3+5H_2O	2·095	Kopp	1509·5	720·53
	2·087	Kopp		723·28
	1·834	Gmelin		823·06

The Sulphate and Chromate of Potash.

KO, SO_3	2·623	Karsten	1091·1	415·97
	2·636	Watson		413·91
	2·662	Kopp		409·87
KO, CrO_3	2·612	Thomson	1241·7	475·39
	2·640	Karsten		470·57
	2·705	Kopp		459·04

Diopside, Hypersthene and Hedenbergite.

$\left(\begin{matrix}3CaO, Si_2O_3\\3MgO, Si_2O_3\end{matrix}\right)$	3·006	Mohs	4408·0	1466·7
	3·127	Mohs		1409·7
$\left(\begin{matrix}3MgO, Si_2O_3\\3FeO, Si_2O_3\end{matrix}\right)$	3·389	Mohs	4657·6	1374·3
$\left(\begin{matrix}3FeO, Si_2O_3\\3CaO, Si_2O_3\end{matrix}\right)$	3·582	Breithaupt	4950·6	1382·1

The crystallized double Sulphates of Potash or Ammonia and Alumina, Peroxide of Iron or Oxide of Chromium.

$\left(\begin{matrix}KO, SO_3\\Al_2O_3, 3SO_3\end{matrix}\right)+24H_2O$	1·724	Kopp	5936·5	3443·4

$\left.\begin{matrix}N_2H_8O, SO_3\\ Al_2O_3, 3SO_3\end{matrix}\right) + 24\,H_2O$	1·626 1·625	Kopp	5673·6	3489·2 3491·4
$\left.\begin{matrix}N_2HO, SO_3\\ Fe_2O_3, 3SO_3\end{matrix}\right) + 24\,H_2O$	1·712	Kopp	6009·7	3510·2
$\left.\begin{matrix}KO, SO_3\\ Cr_2O_3, 3SO_3\end{matrix}\right) + 24\,H_2O$	1·848	Kopp	6295·8	3406·8

The crystallized double Sulphates of Potash or Ammonia and Magnesia, Copper, Iron, Manganese, Cobalt, Zinc, Cadmium or Nickel.

$\left.\begin{matrix}MgO, SO_3\\ N_2H_8O, SO_3\end{matrix}\right) + 6\,H_2O$	1·721 1·696	Thomson Gmelin	2262·5	1314·7 1334·0
$\left.\begin{matrix}CuO, SO_3\\ KO, SO_3\end{matrix}\right) + 6\,H_2O$	2·137	Kopp	2762·8	1292·8
$\left.\begin{matrix}CuO, SO_3\\ N_2H_8O, SO_3\end{matrix}\right) + 6\,H_2O$	1·757 1·756	Kopp	2499·9	1422·8 1423·7
$\left.\begin{matrix}MnO, SO_3\\ N_2H_8O, SO_3\end{matrix}\right) + 6\,H_2O$	1·930	Thomson	2450·1	1269·2
$\left.\begin{matrix}ZnO, SO_3\\ KO, SO_3\end{matrix}\right) + 6\,H_2O$	2·153	Kopp	2770·4	1286·8
$\left.\begin{matrix}NiO, SO_3\\ KO, SO_3\end{matrix}\right) + 6\,H_2O$	2·111 2·136	Kopp	2736·8	1296·4 1281·3
$\left.\begin{matrix}NiO, SO_3\\ N_2H_8O, SO_3\end{matrix}\right) + 6\,H_2O$	1·801 1·783 1·915 1·921	Thomson Kopp	2473·9	1373·6 1387·4 1291·8 1287·8

Apatite, Green and Brown Lead Ore.

$CaCl_2+3(Ca_3O_3,P_2O_5)$	3·15 3·25 3·225	Naumann Mohs	6879·8	2184·1 2116·9 2133·3
$PbCl_2+3(Pb_3O_3,P_2O_5)$	7·0 7·050	Naumann Karsten	16964·6	2423·5 2406·3
$PbCl_2+3(Pb_3O_3,As_2O_5)$	7·2 7·208	Naumann Mohs	18607·9	2584·5 2581·6

By reference to the table now given, it will be seen that our law has received ample confirmation; but it still remains to be explained why the atomic volume in several of the isomorphous groups is not absolutely equal.

The law can obviously hold only for those bodies which are perfectly isomorphous. But this is seldom the case, for those bodies termed isomorphous are generally only approximately so, for we find the angles of their crystals deviating several degrees from one another; neither are the relations between the axes of bodies thus denominated isomorphous perfectly equal. But it is evident, that the more nearly the crystalline forms of isomorphous substances are identical, the more nearly will their atomic volumes be the same. The crystalline condition and atomic volume stand, however, in a certain dependence on one another, which I will endeavour to prove by several groups which have been more closely examined. It may be proper to remark, that the crystallographic notation employed in the following remarks is that of M. Naumann.

It is said that witherite, strontianite, carbonate of lead, and arragonite are isomorphous. They all crystallize in rhomboids, but the dimensions of their angles respectively are not perfectly equal. If we consider the correct atomic volume from each of these bodies as that deduced from the mean of the views already stated, and compare these atomic volumes with the proportions between the axes, the following is found to be the case:—

		Atomic volume.
$Ba\,O, C\,O_2$: a : b : c =	0·7413 : 1 : 0·5950	......286·72
$Sr\,O, C\,O_2$	0·7237 : 1 : 0·6096	......255·53
$Pb\,O, C\,O_2$	0·7236 : 1 : 0·6100	......259·50
$Ca\,O, C\,O_2$	0·7205 : 1 : 0·6215	......213·48

Or we may also compare the atomic volumes with the individual angles, for example with the declinations ∞P and $\breve{P}\infty$:

	$\infty P =$	$\breve{P}\infty =$	Atomic volume.
$Ba\,O, C\,O_2$:	118° 30′		286·72
$Sr\,O, C\,O_2$:	117 16	108° 12′	255·53
$Pb\,O, C\,O_2$:	117 14	108 13	259·50
$Ca\,O, C\,O_2$:	116 16	108 27	213·48

From these comparisons it is shown that the carbonates of lead and strontia are perfectly isomorphous: their atomic volumes also approximate very closely. Again, it is seen that the two other bodies are neither isomorphous with one another nor to the former minerals: hence we find that their atomic volumes also differ.

But it is also apparent that an increase of atomic volume for this group must be followed by an increase of the axis *a*, and a decrease of the axis *c*; or according to the augmentation in the atomic volume the declination ∞P must become more, and the declination $\breve{P}\infty$ less obtuse.

If one of these crystals (of arragonite for example) be heated, its density becomes less, and in consequence of this its atomic volume greater. The consequence of this must be that the declination ∞P must be more and that of $\breve{P}\infty$ less obtuse; and this has been long since observed to be really the case.

But the relation between the crystalline form and the atomic volume may be more correctly estimated in another class of carbonates.

The carbonates of zinc and magnesia, mesitine, the carbonates of iron and manganese, dolomite and calcareous spar, are a group of bodies which possess both an analogous constitution and an equivalent crystalline form. The crystalline form of all of them is that of a rhombohedron, but the axes a in them are unequal and the angle R different. If we adopt the mean of the observations already given as the atomic volume of each of these bodies, we find that the axis a of the rhombohedron increases, that the angle R diminishes, whilst the atomic volume increases.

	Axis a.	Angle R.	Atomic volume.
Carbonate of zinc	0·80708	107° 40′	175·33
Carbonate of magnesia	0·81165	107 25	181·25
Mesitine..................	0·81498	107 14	186·26
Carbonate of iron	0·81962	107 0	188·50
Carbon. of manganese	0·82182	106 51	202·29
Dolomite	0·83312	106 15	202·36
Calcareous spar.........	0·85440	105 15	231·20

We wish to establish a connexion between the length of the axis a and the atomic volume of a body; for this purpose it is natural to assume the atomic volume as the volume or the cubic capacity of its fundamental form. Accordingly, in the group now considered, the atomic volume (V) must be proportional to the length of the axis a; hence we have

$$a = y\mathrm{V}.$$

But another number is found for y in every body, and the cause of this is obvious. It is supposed in this formula, that the filling up of the space in the rhombohedral crystals is equal on all sides; but it is known by the optical characters of these crystals that this is not the case. In order to discover a relation between a and V, let us suppose

$$a^x = y\mathrm{V}.$$

We seek x and y according to the method of the least squares from the estimations of a and V of the seven different substances, and we find

$$x = 4{\cdot}739 \qquad y = 0{\cdot}0020417.$$

The relation between a and V is therefore

$$a^{4{\cdot}739} = 0{\cdot}0020417\ \mathrm{V}.$$

This formula coincides very exactly with the observations. And as the greater part of the substances in their natural condition are accompanied by impurities, the formula may be employed to calculate their specific weight from their crystalline form. If we suppose that the axes of the bodies already examined are given, we deduce the atomic volume, and from it the specific gravity.

	Atomic volume.	Spec. gravity.
Carbonate of zinc.........	177·37	4·3956
Carbonate of magnesia...	182·18	2·9355
Mesitine	185·75	3·3658
Carbonate of iron.........	190·41	3·7585
Carbonate of manganese	193·26	3·7377
Dolomite	210·28	2·7755
Calcareous spar	232·36	2·7220

From the differences occurring between the specific weight observed and calculated, we can conclude whether the substances found in their natural condition are rendered impure by substances specifically heavier or lighter; but with those minerals which occur in a state of purity, the specific gravities ascertained by observation and calculation approximate very closely. In the case of dolomite the specific weight obtained by experiment is always greater than it is found to be by calculation; but analysis shows that it is always rendered impure by the oxides of iron and manganese. The carbonate of manganese is, on the other hand, less than the calculated result, but it is always mixed with carbonate of lime.

From what has now been brought forward, it must be evident that an increase of atomic volume is dependent upon an increase of the axis a. The application of heat to one of these crystals must decrease its density, and the axis a must be enlarged, whilst the angle R will be rendered less obtuse.

This has long since been discovered by Mitscherlich. This chemist has accurately determined the diminution of density on the application of heat to calcareous spar. He found that by a heat of 100° C. (180° F.) its specific gravity was decreased in the proportion of $1 : \frac{1}{1\cdot001961}$. We find above the specific weight of calcareous spar, when its axis $a = 0\cdot85440$ and its angle $R = 105° \; 5'$ is 2·7220. By heating it for 100° C., therefore, it will be equal to 2·71675, or its atomic volume passes from 232·36 to 232·80. If we determine the length of the axis a by means of the formula already given, we find it $= 0\cdot85672$, corresponding to an angle R of 104° 57′ 22″. According to this calculation the change in the angle R by 100° C $= 7' \; 37''$, a result which coincides sufficiently with that found directly by Mitscherlich (8′ 34″), when we consider the difficulties which necessarily accompany the direct measurement of the dilatation and change of the angles.